

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	GC(a)	<p>Despite the limitations of the Pilot Study, The results of the Pilot Study suggest that several tools are available to collect useful data regarding transition zone water quality (Trident, GeoProbe, and Small Volume Peepers) at different types of sites. EPA recommends use of one method (i.e., small volume peepers) everywhere (fine, sandy and coarse grained areas) and to use them at depth in the fine grained areas. Volatile organic compounds (including some of the more mobile semivolatile compounds such as naphthalene) should be sampled through the use of peepers. In areas where sediment texture allows its use, the Trident Probe should be installed along with the small volume peepers to develop and understanding of the variability between the two methods and allow characterization of data uncertainty.</p> <p>Areas to be sampled with the Trident Probe should include both the shallow (30 cm) and deeper (90 cm) data. To the extent feasible, small volume peepers should also be installed at depth in the fine grained areas. This depth information will allow us to better understand how groundwater plumes are entering the Willamette River.</p>	<p>LWG responded to the first portion of this comment, relating to utility of the Trident Probe and small volume peepers (SVP) in a letter to EPA dated August 29, 2005. This letter provided additional technical discussion of sampling method reliability and the potential for sampling bias using the Trident Probe and SVP. This additional technical discussion has also been added to the FSP in Sections 2.3 and 2.4.</p> <p>Based on subsequent discussions with EPA and its agency partners, paired deep Trident samples were included in the Round 2 Groundwater Pathway Assessment sampling program at selected locations. It is not practical to install the small volume peepers at depth greater than 38 cm (total depth of the sampling device) because the required excavation would cause significant sediment disturbance and loss of the fine sediment material. These agreements are documented in detail in the revised Addenda to this Transition Zone Water Sampling FSP.</p>

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	GC(b)	A conceptual three dimensional understanding of the groundwater plumes in river is critical in order to assure appropriate placement and density of groundwater discharge mapping and water quality sampling locations. This understanding is also critical in interpreting groundwater data. The interpretation of the results of the pilot studies and future discharge mapping and transition zone sampling at the nine Round 2B groundwater sites would benefit by providing appropriate figures in the report showing how each upland groundwater plume projected into the river (e.g., plan view maps and geologic cross-sections). These figures should be based on all available data and geologic conditions. This type of presentation would allow the regulatory team to view the data in terms of the hydrogeologic conceptual site model.	To address this concern, LWG developed updated cross-section figures for each site that depict the most recent observations of groundwater COI concentrations. These are presented in Addendum 1 and Addendum 2 to this Transition Zone Water Sampling FSP. This additional information was considered, along with plan view plots of upland groundwater COI observations and discharge mapping results, in development of the site-specific TZW sampling plans presented in the Addenda.
A1	GC(c)	Although the use of filtered water samples may be useful for analyzing method performance, EPA has repeatedly stated that unfiltered water samples will be used for the data interpretation.	Comment noted. It is anticipated that filtered sample data will provide important interpretive information on the topic of actual COI mobility vs. sampling method-induced apparent COI mobility.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	GC(d)	<p>Given the observed variability in the Pilot Study results, transition zone water sampling results below detection limits or levels of concern may not give us confidence to conclude that groundwater COIs are not impacting the Willamette River.</p> <p>In addition, at some locations, deeper groundwater plumes discharging farther out into the Willamette River may not be picked up by the TZW sampling. For example, data collected offshore of the acid plant at Arkema (Supplemental Figure 11) shows the highest concentrations of chlorobenzene just west of the north end of Dock 1 at minus 28 to minus 22 feet (WB10). The TZW sampling performed as part of the Pilot Study occurred 75 to 100 feet to the north and south of this high concentration area. As it result, samples taken east of WB-10 at a deeper depth in the river might easily have shown much higher levels of chlorobenzene in the TZW had they been collected because the deeper plumes are discharging farther out.</p>	<p>The pilot study results show that the selected tools (SVP and Trident) were able to detect COIs in transition zone water in groundwater discharge areas and showed very good reproducibility among replicates, with the exception of one replicate location at the Acid Plant area. Sampling method performance (reproducibility and reliability, along with practical considerations for implementation and other methodological issues) are discussed extensively in Section 2 of the revised FSP. Analytical concentration goals for the Round 2 Groundwater Pathway Assessment were developed in coordination with the agency team to maximize the likelihood that detection limits are sufficiently low to identify COIs in transition zone water at concentrations that may contribute to unacceptable risk to in-water receptors. Finally, the extensive discharge mapping work and the multiple lines of evidence approach for selecting sample locations for the Round 2 Groundwater Pathway Assessment were designed to ensure that sample collection is targeted in areas of possible groundwater plume discharge to the river. For these reasons, the LWG believes that the Round 2 Groundwater Pathway Assessment will provide reliable estimates of concentrations of chemicals in transition zone water in groundwater discharge areas.</p> <p>The discharge mapping and TZW sampling program was designed to identify and characterize potential groundwater plume discharges to water depths up to 40-50 feet. Round 2 Groundwater Pathway Assessment sampling activities were not designed to delineate plumes which extend below the bottom of the channel. Further discussions are needed between LWG and the agency team regarding the relevance of deeper plumes for the in-water RI/FS and the ecological and human health risk assessments</p>
A1	GC(e)	<p>EPA may require, based on an evaluation of the TZW data, the collection of off-shore GeoProbe groundwater data to complete the characterization at locations where there is a lot of uncertainty about the contaminant plume distribution and where the plume may be discharging to surface water. Further evaluation of the data will also be required to determine whether it is sufficient for evaluating risks to human health and the environment.</p>	<p>Comment noted. Please see the LWG's letter of July 25, 2005 memorializing agreements reached during final scoping of the Round 2 Groundwater Pathway Assessment.</p>

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(1)	Section 2 – Analysis of Pilot Study Transition Zone Water Sampling Methods: EPA concurs with some of the practical limitations identified in this section such as the inability of the Trident Probe to collect transition zone water from fine grained sediments. In addition, the mechanical installation method seems to be the critical selection criteria for the different tools. From the descriptions it seems that the Small Volume Peepers, the Trident, and the GeoProbe were the only tools that worked routinely. The additional discussion on the other tools seems to be somewhat irrelevant if the technique is not expected to be useful in a large field exercise. The rest of the discussions and the related analysis should be minimized to concentrate on the more useful tools and results.	Discussion of all of the tools evaluated in the pilot study is necessary in Section 2 of this FSP, as this is the agreed-upon document for presenting these pilot study findings and the associated analyses/interpretation. As such, the discussion will be left in place for Section 2. Reference to methods considered inapplicable based on the analysis presented in Section 2 (large-volume peepers, vapor diffusions samplers, UltraSeep sampling, and power grab/centrifugation) will be removed from Section 3, where the transition zone water results are discussed in the context of characterization of each study site. This will eliminate redundant discussion of the inapplicability of these tools.
A1	SC(2)	Section 2.2.6 – Power Grab/Centrifuge Separation Samples: There are obvious practical limitations associated with the Power Grab sampling technique due to the delay in processing the samples and the resulting samples. Furthermore, this method would be of little value for volatile organic compounds due to the high potential for loss of contaminants. Overall, the concept of taking a sediment sample and then centrifuging it to obtain a water sample (by mobilizing and separating the water fraction in that sample) is functionally different from the EPA suggested method of sampling with the Trident or GeoProbe tools, in which using a low-flow sampling technique avoids mobilizing sediment particles into the water samples. EPA recommends that this method not be considered any further for comparison with ground water or transition zone samples.	Agreed. This comment agrees with the conclusions of the pilot study regarding the power grab/centrifuge sampling of transition zone water, as presented in this FSP.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(3)	Section 2.3 – Intra-Method Evaluation (Method Reproducibility): Given the large variability in the results from the pilot study and limited sampling results, a detailed statistical analysis of the data has limited usefulness. The more interesting factor is that the sampling did produce a large number of detects, which may be variable for a number of field sampling reasons. More detailed work, such as more “duplicate” and “replicate” samples in an area may be much more useful than to do statistical analysis on this limited data set.	The statistical tests used in this evaluation are applicable to the data sets collected, and LWG stands by their application and interpretation. LWG responded to this comment, regarding reproducibility of the Trident Probe and SVP results in a letter to EPA dated August 29, 2005. This letter provided additional technical discussion of the reliability and potential for sampling bias using the Trident Probe and SVP, also noting the resulting implications for study design of the sampling program. This additional technical discussion has also been added to the FSP in Sections 2.3 and 2.4.
A1	SC(4)	Section 2.3.2 – Data Processing: The usefulness of a correlation analysis on detected vs. non-detected results is questionable. The usefulness of this analysis should be clarified or deleted from the report.	This analysis is noted as a first-level analysis in the text. It provides a simple first look at the data sets. Interpretations of results are based on multiple analyses as well as in-field observations of implementability, etc.
A1	SC(5)	Section 2.3 – Intra-Method Evaluation: Equations for the correlation coefficients should be provided.	The equations will be added to the revised text in Section 2.3.
A1	SC(6)	Section 2.3.3 – Intra-Method Evaluation Results and Table 2-2: Table 2-2 provides a very general summary of the method evaluation results (by study area and by sampling method). This ignores the fact that the sampling methods may result in more reproducible results for certain classes of compounds and that not all samples were submitted for the same analytes. The summary of results presented in Table 2-2 may not be a fair evaluation of the data. A more detailed intra-method analysis that breaks out results by analytical method and focuses on the differences associated with sediment material type should be provided.	<p>These tests provide an assessment of the overall tool reproducibility at each study site. They are not meant to identify tool reproducibility by analyte group. LWG submitted a letter to EPA on 8/29/05 clarifying the analysis of reproducibility to address EPA concerns. The text in Sections 2.3 and 2.4 has also been edited to incorporate the language from this letter.</p> <p>Additionally, to clarify analyte lists for each sampling tool for each site, a generalized summary table of pilot study sampling tools and associated analyte groups has been added to the FSP (inserted as Table 2-1). This information is also presented, in greater detail, in the Pilot Study Data Report (Appendix B to the SAP).</p>
A1	SC(7)	Section 2.4 – Inter-Method Comparison of Chemical Results: Some justification for setting non-detects to zero and not some other value, such as half the detection limit, should be provided.	Due to several factors including varying volumes of water provided by each sampling method, the detection limits varied widely among samples for the same analyte. As such, use of the detection limit or some fraction of the detection limit would have confounded the analysis and consistently biased the results to the reported detection limit values. Therefore, use of zero for undetected results in these analyses was the best assumption for the purposes of statistical analysis. A few sentences have been added to the text to clarify this.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(8)	Section 2.4 – Inter-Method Comparison of Chemical Results: Please provide the list of “chemicals detected by only one or by none of the methods of a given location” that were excluded for analysis.	The list of included and excluded analytes has been added as Table 2-4a.
A1	SC(9)	Section 2.4 – Inter-Method Comparison of Chemical Results: Please provide separate analyses of the PAHs to differentiate the more mobile low molecular weight PAHs (LPAHs) from high molecular weight PAHs (HPAHs).	Inter-method comparison of LPAHs and HPAHs has been added to Table 2-4b (formerly Table 2-3).
A1	SC(10)	<p>Section 2.4.1 – The assumption that the samples are co-located makes the interpretations suspect. Sample locations in the field may be several feet away from each other and may have been sampled using different methods.</p> <p>The more important results are the significant number of samples with detected concentrations, indicating that contamination in the transition zone water is present at many locations, at many different concentrations, and that it can be detected with different tools.</p>	<p>Assumption of approximate co-location is inherent in a comparative analysis of results between methods. It is clear in the text that this assumption is not completely met; however, exact co-location of sample collection by the various methods was not possible. Samples were targeted for co-location to the extent possible, and it was recognized that there would be some variability in station positioning.</p> <p>A fundamental goal of the pilot study was to evaluate and select methods for use in the Groundwater Pathway Assessment. These statistical analyses offer important insight into and confidence in method selection.</p>
A1	SC(11)	Section 2.4.1 – Inter-Method Statistical Analysis and Table 2-3: It appeared that not all methods were used for all chemical classes at all sites. Please indicate in Table 2-3 which methods were not used/compared in the statistical analysis.	The statistical analyses could not be performed for all analyte groups and all methods because not all analyte groups were sampled by every method (e.g., VOCs could not be sample by sediment centrifugation). To clarify this, a table has been added (now Table 2-1) which presents analyte groups sampled by each method at each site. Additionally, Table 2-3 has been clarified.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(12)	<p>Section 2.4.1.1 – ARCO and Figure 2-8: Please separate the LPAHs and HPAHs.</p> <p>In this figure, presenting the data in quartile ranges with an exponential scale appears to obscure interpretation of the data and is not necessary as the “extremely outlying values” appear to be less than 10 ug/L. Please present the data in the format of Figures 2-9 and 2-10 for LPAHs and HPAHs separately.</p> <p>In addition, certain elements of the evaluation should be clarified. For example, there does not appear to be any unfiltered large-volume peeper results presented, and TPH results were not compared.</p>	<p>Figure 2-8b and 2-8c have been added to present the LPAHs and HPAHs separately.</p> <p>The logarithmic scale was used to present this data because it ranges over more than four orders of magnitude. The data would be truly obscured if presented on a linear scale. Additionally, the quartile ranges offer more information about the distribution of the data than a simple bar graph could. A simple bar graph, as presented in Figure 2-9 and 2-10 for metals and TPH, only indicates a single value, and for a group of values such as PAHs, it would only indicate the highest value. To provide added information about the data distribution, values more than three times the interquartile range are presented as outliers. The term outlier is not used to indicate suspicion that a value that is incorrect or that it does not belong in the data set; it is merely an indicator of where the data point falls when the data set is viewed as a distribution.</p> <p>To clarify this, a table has been added (now Table 2-1) which presents analyte groups sampled by each method at each site. To answer the specific concerns raised: (1) unfiltered LVP samples were only collected at the ARCO site for VOCs and TPHg, because excessive amounts of sediment were present in the sampling vessels when retrieved (noted in Table 2-1); (2) TPH results are presented in Figure 2-10.</p>

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(13)	<p>Section 2.4.1.2 – Acid Plant and Figure 2-11: Please identify all compounds that are the “outlying values” and “extremely outlying values.”</p> <p>Provide a separate analysis of individual VOCs that are consistently identified as an “extremely outlying value,” such as MCB, chloroform, methylene chloride, benzene.</p> <p>Please also indicate on the figure the sediment characteristic that was found at each sample location.</p> <p>Further clarification of what is meant by “not significantly different” in the statement “Trident and small-volume peeper results were not significantly different for VOCs” should be provided. There appears to be quite a bit of variability in the data.</p>	<p>Figure 2-11 has been edited to indicate all outliers.</p> <p>Additional text has been added to discuss the VOCs, per the LWG’s letter to EPA dated 8/29/05.</p> <p>The sediment texture had been added to Figure 2-11 and other similar figures.</p> <p>The phrase “not significantly different” refers to the result of the statistical inter-method analysis. The threshold value of $\alpha = 0.05$ from the Mann-Whitney U Test was used to define significance. Additional text has been added to this discussion, per the LWG’s letter to EPA dated 8/29/05.</p>
A1	SC(14)	<p>Section 2.4.1.2 – Acid Plant and Figure 2-12: In the second paragraph, please state that there is no unfiltered Trident manganese result nor small-volume peeper manganese result. The use of the phrase “all methods” is misleading.</p> <p>Please indicate on the figure the sediment characteristic that was found at each sample location.</p>	<p>To clarify this, a table has been added (now Table 2-1) which presents analyte groups sampled by each method at each site. Additionally, the text has been clarified in this section.</p> <p>The sediment texture had been added to Figure 2-12 and other similar figures.</p>
A1	SC(15)	<p>Section 2.4.1.2 – Acid Plant and Figure 2-13: Please indicate on the figure the sediment characteristic that was found at each sample location.</p> <p>Based on Figure 2-13, it appears that unfiltered large volume peepers have higher concentrations in what we understand are the siltier sediments. This should be discussed in the text.</p>	<p>The sediment texture has been added to Figure 2-13 and other similar figures.</p> <p>Unfiltered large volume peeper samples at the Arkema site do have higher results for the AP04B and AP04D, which are siltier than AP03B. There is, however, no basis to infer a trend from this, given AP04D is significantly siltier than AP04B, while the DDX concentrations at AP04D are much lower than AP04B (and only slightly higher than the SVP results at the same location). It may be that the variability is a function of the amount of sediment collected with the samples, which was a general confounding factor in the large volume peeper dataset.</p>

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(16)	<p>Section 2.4.1.3 – Chlorate Plant and Figure 2-14: Please indicate on the figure the sediment characteristic that was found at each sample location.</p> <p>In the second paragraph, make explicit (not as the last sentence of the paragraph) that there are no unfiltered large volume peeper results for sample location CP07B. Without this statement closer to the first sentence, the topic sentence: “[t]he Trident showed higher concentrations than other methods for total chromium (both filtered and unfiltered)” is misleading. In fact, it appears that unfiltered large volume peepers have higher chromium concentrations in what we understand are the siltier sediments.</p>	<p>The sediment texture had been added to Figure 2-14 and other similar figures.</p> <p>This section of text has been clarified.</p>
A1	SC(17)	Figure 2-17. It is not clear why this figure does not include all the different sampling techniques for a full comparison. For example, surface water and Power Grab samples were not included for comparison.	Small volume peeper results were added to this figure. Additionally, the figure showing the Stiff Diagram for surface water and the upland groundwater samples (formerly Figure 3-2) has been moved up to become Figure 2-18, to provide context for the supporting discussion. Finally, conventional analytes (major ions) were not analyzed as part of the Power Grab/Centrifuge work. This is clarified with the addition of Table 2-1.
A1	SC(18)	Section 2.5 – Effects of Filtration: Although filtered data may be useful for assessing method performance, it should be noted that filtered data will not be utilized for assessing the risk to human health and the environment associated with transition zone water data.	See response to comment GC(c) above.
A1	SC(19)	Section 2.6 – Effects of Centrifugation: It should be noted that solubility limits for individual PAHs are typically derived in a laboratory setting using clean water. Effective solubilities of PAH mixtures are influenced by the mole fraction of the PAH mixture and may be substantially different than the solubilities presented in this analysis.	The text has been edited to clarify that the solubility values used in this presentation of information are for pure phase of the compound in pure water. A note has also been added to indicate the many factors that can affect solubility of PAHs including salinity of the aqueous solution, possible cosolvency effects, temperature, mole fraction of the PAH in the organic mixture, the overall hydrophobicity of the organic liquid mixture relative, and the potential role of colloids enhancing apparent solubility.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(20)	Section 2.7 – Major Ion Analysis: At both pilot study locations, LWG draws the conclusion that “the transition zone water samples collected by the large volume peeper may have been influenced by river water.” Further explanation for the unfiltered large volume peeper results for pesticides at AP-04B and AP-04D and chromium at CP-06C and CP-08D is required. In this instance, large volume peepers had the highest pesticide and chromium concentrations, respectively, over the other methods (see Figures 2-13 and 2-15). As stated in our general comment above, the limited nature of the Pilot Study limits the conclusions that may be drawn from the large volume peeper data set.	For Arco, the suspicion of river water presence in the large volume peeper (LVP) samples is based primarily on the Piper Diagram presented in Figure 2-17, where LVP results fall closer to the surface water major ion distribution than those of groundwater. For the Arkema site, the concern is based on the relatively low overall salinity observed in the samples (especially relative to that observed in Trident samples). These are not definitive conclusions, and the text indicates this uncertainty. This conclusion, however, is not refuted by the pesticide and chromium concentrations observed in the unfiltered LVP samples. These concentrations are likely due to equipment limitations which resulted in sediment entry into the LVP samplers, thereby making the samples unrepresentative of transition zone water. Highly soluble analytes (i.e., major ions) provide better signatures of the origin of the water in the sample, when there is also the confounding issue of the presence of sediment in samples. This is discussed further in the text.
A1	SC(21)	Section 2.8 – Recommendations for Method Selection: Evaluations of chemical concentrations and sampling methods in Section 2 do not discuss the sampling methods in terms of their efficiency in “coarse-grained sediments” versus “fine-grained sediments.” Additional justification for why “the Trident is the most applicable...for coarse-grained sediments” and “the small-volume peepers are an effective tool for fine-grained sediments” should be provided. The data as currently presented do not appear to support these conclusions. In addition, the use of GeoProbe sampling devices should be considered in the suite of recommended techniques. GeoProbe sampling represents a potential tool for depths of 2 feet or deeper into the sediment and is at least as reliable as the Trident Probe.	The data and practical observations (low purge rates for Trident in fine-grained sediment; loss of fines during excavation of coarse-grained material for peeper installation) support the conclusions about the applicability of the tools in various sediment textures. Additional information provided in a letter to EPA, dated 8/29/05, has been added to the text to further clarify. The Trident tool was modified to allow for sampling to depths of up to 150 cm (5 ft). The tool was applied to this depth, in accordance with conditional FSP approval by EPA. It should be noted that there is no technical evidence presented by EPA for the comment that the GeoProbe is “at least as reliable as the Trident Probe”. There are technical concerns about infiltration of river water into casings during sampling and about the ability of the GeoProbe to collect transition zone water samples at shallow depths below the mudline (at the depths of biological activity).
A1	SC(22)	Sections 3.1.3 Metals, 3.1.4 Petroleum Hydrocarbons, 3.1.5 BTEX and MTBE, 3.1.6 Polycyclic Aromatic Hydrocarbons: These sections would greatly benefit from a summary table to present the results by contaminant class (including upland concentrations) and if possible, a figure to show upland and in-water sampling locations.	This information is presented on cross-sections and plan-view figures in Addenda 1 and 2 to this FSP.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(23)	Section 3.1.4 – Petroleum Hydrocarbons. There is no clear definition and laboratory method reference for the “TPH—R”. The concept of “residual” product is a source of much debate and extrapolation for conclusions as it relates to hydrogeologic contaminant fate and transport. While it is defined as “residual” in the text, it is not clear what the definition of that is, or what method is used to analyze it. TPH data should be referred to as the more common TPH categories – TPH-G and TPH-Dx (diesel range extended which will include the residual range TPH).	Presentation of TPHg, TPHd, and TPHr provides additional information about the distribution of TPH chemicals in the samples. The analytical methods, which define the ranges, are described in the QAPP.
A1	SC(24)	Section 3.1.6.2 – PAH Equilibrium Analysis: EPA has a number of comments regarding the PAH Equilibrium Analysis provided in this section. These comments also apply to the “DDX” equilibrium analysis presented in Section 3.2.3.2 and are summarized below:	The following comment responses address the comments for both the PAH and DDX equilibrium discussions and figures.
A1	SC(25)	It is not clear why there is so much emphasis on the estimation of equilibrium. The values for K_{ow} and K_d are very difficult to determine, and are based on a laboratory estimate based on one chemical, one sediment type, and optimum laboratory conditions. Those are not necessarily the same conditions encountered in contaminated sediments or aquifers, where the contamination is commonly from mixed sources or compounds, which by their combined characteristics can alter the K_{ow} and K_d parameters. The emphasis on this field work should be in obtaining sufficient field data to avoid the need to be estimating parameters or concentrations. Note the first sentence in the section “Under certain idealized conditions.....” Because Willamette River sediments are not under such conditions, evaluations that consider equilibrium conditions should be revised to reflect this fact or qualified appropriately.	In discussions during scoping of the groundwater pathway assessment, EPA raised concerns about the potential for disequilibria between sediment and transition zone water, particularly in areas of active groundwater advection. Further, in the recent EPA Draft <i>Identification of Round 3 Data Gaps</i> (12/2/05), EPA indicated that contaminant loading may be estimated through an equilibrium partitioning approach. As such, an evaluation of the pilot study sampling results to compare observed and theoretical partitioning behavior is warranted. Additionally, it seems reasonable to compare these values to published K_{oc} values. LWG understands that the conditions of the Willamette do not match the exact conditions under which the published K_{oc} values were derived. This is noted in the text. As suggested in comment SC(30), additional published K_{oc} values were added to the analysis to provide a range of published values for comparison. Additionally, the text has been edited to clarify the intent of this comparison and the limitations on conclusions, given the size of the dataset.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(26)	Back calculation of equilibrium partitioning coefficients, which are typically measured in a closed container with a known volume of water and soil/sediment material, may not be appropriate. In the environment, there are other physical phenomena in effect such as groundwater movement through the sediment that are not accounted for in this back calculation.	Agreed. The text and figures have been revised to clarify that the observed ratios between aqueous and solid-phase concentrations do not necessarily reflect equilibrium conditions. See comment response SC(25).
A1	SC(27)	The report should provide the f_{oc} values used in the calculations. Were the values used average concentrations based on historic sediment data used or site specific concentrations that account for the differences between coarse-grained sand and silt.	The f_{oc} values used in the partitioning calculations were from sediment samples collected by the power grab device during the pilot study. These samples were co-located (as well as station positioning allowed) with the relevant TZW samples. As such, it is reasonable to assume that these inherently account for site-specific conditions and grain size. The f_{oc} values have been added to the text as footnotes in Sections 3.1.6.2 and 3.2.3.2.
A1	SC(28)	<p>The PAH analysis evaluates individual PAHs against each individual partitioning coefficient. However, this evaluation does not account for the effects of mixed contaminants in the environment and how mixtures change the characteristics of individual PAHs. Equilibrium conditions are not necessarily expected in the transition zone. However, we would expect that the flushing action of groundwater discharge to surface water and other physical actions would cause contaminants with higher solubilities and lower K_{oc}s to move to surface water. As stated above, a lower aqueous concentration (potentially from mobility) would result in an inaccurate higher K_{oc}.</p> <p>We do not accept the conclusion that “the system favors partitioning of the low molecular weight PAH compounds to sediment.”</p>	<p>LWG agrees that the conditions in the sediment are not necessarily at equilibrium. The text and figures have been revised to clarify that the observed ratios between aqueous and solid-phase concentrations do not necessarily reflect equilibrium conditions. The comparison of observed partitioning to published K_{oc} values was made to begin to investigate this condition.</p> <p>This statement has been replaced with, “observed concentrations of higher molecular weight PAHs at the ARCO site are lower than would be predicted by applying published equilibrium K_{oc} values to measured bulk sediment concentrations and f_{oc} values.”</p>

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(29)	The conclusion in the last paragraph should be further supported – an alternative explanation to the data distribution could be the difference in sampling methods (i.e., why are the Trident results plot only in the upper right hand portion of the figure?).	Discussion has been added to the text about the possible effect of the different sampling methods. Note: The Trident values are only present for the lower molecular weight compounds in the PAH figure because the results were below detection limits for the higher molecular weight compounds. A note has been added to the figure to call this out.
A1	SC(30)	Koc values from EPA's soil screening guidance for estimation of PAH partitioning in sediment and groundwater should not used. The EPA (2003) <i>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures</i> contains calculations of Koc values appropriate for use in sediment. Figure 3-3 should be redrawn to include Koc values appropriate for use with sediments. As it is, Figure 3-3 indicates that the soil-derived Koc values are between measured K _{oc} values for all compounds plotted except phenanthrene, fluorene and acenaphthene. At the very least, Figure 3-3 illustrates that the estimated site-specific K _{oc} values bracket literature K _{oc} values for 7 of the 10 chemicals illustrated. EPA does not agree with the LWG's contention that the use of equilibrium partitioning calculations consistently overestimates chemical concentrations in transition zone water.	K _{oc} values from EPAs soil screening guidance and from EPA (2003) <i>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures</i> are now presented on Figure 3-2 (was figure 3-3) and Figure 3-5 (was Figure 3-6) to show a range of published K _{oc} values. It is interesting to note that the published K _{oc} values for the PAHs do not differ greatly here; however, for the DDX compounds, there is a wide range. The text interpreting the comparison of observed partitioning values and published K _{oc} values has been edited and clarified.
A1	SC(31)	Figure 3-3 is unclear. If the point of the plot is to show that the values detected are above the literature values of K _{oc} , then there needs to be much more explanation about the development of the K _{oc} values in the literature, and how the values for the ground water samples may be affected by not being a simple compound under optimum lab conditions. In addition, the data presented should include a range for the Koc values, and not just one single literature value. This comment also applies to Figure 3-6.	See comment responses SC(25) through SC(30).

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(32)	Section 3.1.7 – Summary of Pilot Study Findings – ARCO Study Area, Second Bullet Unless additional justification is provided, delete the second sentence of the second bullet.	The statement relating to large-volume peeper samples has been removed as part of comment response SC(1), by which discussion of methods other than Trident and small-volume peepers was removed from Section 3.
A1	SC(33)	Section 3.1.7 – Summary of Pilot Study Findings – ARCO Study Area, Fifth Bullet Add the word “individual” before water solubility limits.	The statement relating to power grab/centrifuge samples has been removed as part of comment response SC(1), by which discussion of methods other than Trident and small-volume peepers was removed from Section 3.
A1	SC(34)	Section 3.2.3.2 – DDT, DDD, and DDE: Please add the groundwater sampling locations onto the supplemental figures.	Upland groundwater sampling locations and results for Arkema are now presented on plan view and cross-section figures in Addendum 1 to the FSP.
A1	SC(35)	Sections 3.2.4.1 – Perchlorate, 3.2.4.2 Total Chromium: These sections would greatly benefit from a figure in this attachment to show upland and in-water sampling locations.	Upland groundwater sampling locations and results for Arkema are now presented on plan view and cross-section figures in Addendum 1 to the FSP. Additionally, in-water sampling locations from the pilot study are presented in Figures 2-1 (ARCO), 2-2 (Acid Plant), and 2-3 (Chlorate Plant) of this FSP.
A1	SC(36)	Section 3.2.5 – Summary of Transition Zone Water Sampling Results – Arkema Acid Plant and Chlorate Plant Study Areas: In the second bullet, further discussion of the chlorobenzene transition zone water concentrations relative to “the heart of the chlorobenzene plume” in comparison with the methylene chloride and chloroform transition zone concentrations which were substantially higher than observed in upland groundwater. Similarly, in the third bullet, further discussion and/or justification are required with respect to statements such “.... Transition zone water at this location may not be related to groundwater discharge and may be related to sediment contamination.”	The text has been clarified to the extent that information is available regarding comparison of the pilot study TZW results with historical Arkema in-water GeoProbe® sampling results.
A1	SC(37)	Section 4.1 – Approach to Selection of Transition Zone Water Sampling Locations: The inclusion of deeper water sampling results in the pilot study was a benefit to the evaluation of the information. This highlights the need for additional sampling of deeper groundwater either as part of this effort using the Trident Probe or in future sampling events using a GeoProbe or similar sampling device.	Per agreement with EPA and its agency partners, deeper transition zone water sampling (up to 150cm [5ft]) was added to the FSP. A custom intake was manufactured for the Trident probe to allow for this deep sampling. Please see the LWG’s letter of July 25, 2005 regarding potential future application of Geoprobe in the Groundwater Pathway Assessment.

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(38)	Section 4.1 – Approach to Selection of Transition Zone Water Sampling Locations: In addition, to the proposed summary, EPA expects LWG will provide, prior to the review period, revised figures that were commented on as part of the SAP comments and that show the projection of groundwater contaminant plumes into the Willamette River.	Stratigraphic cross-sections for each site were updated to include groundwater COI concentrations. These are presented in Addendum 1 and Addendum 2 to this FSP. These were utilized in the lines of evidence approach to sample selection. A bullet has been added to Section 4.1 of the FSP, thereby including these figures in the list of items to be used in sampling location selection.
A1	SC(39)	Section 4.1 – Approach to Selection of TZW Sampling Locations: The paragraph at the bottom of the page states that “a minimum of four and a maximum of 15 water sampling locations will be considered for each site.” It is unlikely that four samples will be acceptable at any site. The site specific work plans should include the specific rationale and objectives of each sampling location.	The statement has been edited to read “a minimum of six...”, which reflects the agreements between EPA and LWG for conditional approval of each of the subsequent Addenda to this FSP. The Addenda provide the rationale and sampling objectives for each location, as specified by this comment.
A1	SC(40)	Section 4.1 – Approach to Selection of TZW Sampling Locations: The paragraph at the bottom of page 33 states that “...typically...one sampling location within each identified groundwater discharge zone...” will be sampled at 90 cm. The site specific work plans should include the specific rationale and objectives of each sampling location.	The Addenda provide the rationale and sampling objectives for each location, as specified by this comment. Additionally, “at least” has been added to the noted sentence.
A1	SC(41)	Section 4.2 – Sampling Methods: Based on the information presented in this draft, low volume peepers should be used to sample VOCs (including some of the more mobile semivolatile compounds such as naphthalene). Peepers should be deployed at all locations where these classes of compounds are expected and in siltier locations as described in the TZW FSP. Based on the results of the Pilot Study, EPA does not believe that the Trident method is as reliable for volatiles and more mobile compounds.	LWG responded to this comment in a letter to EPA dated 8/29/05 and provided additional supporting rationale for the reliability of the Trident Probe to sample VOCs. EPA agreed with the LWG’s proposed approach for sampling VOCs in its conditional approval of specific sampling plans presented in Addendum 1 and Addendum 2 to the FSP (conditional approval letters received on 9/30/05 and 10/13/05). Additionally, the text of this FSP has been augmented with additional discussion to support the conclusion that the Trident is equally reliable as the small-volume peepers, when applied appropriately. See comment response GC(a).

LWG Response to EPA Comments

Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan: Attachment 2: Field Sampling Plan - Transitions Zone Water Sampling

Attachment 2: Field Sampling Plan – Transition Zone Water Sampling

Comment No.		EPA Comment	LWG Response
A1	SC(42)	<p>Section 4.3 – Chemicals of Interest and Table 4-1:</p> <p>Additional chemicals should be included on the list of COIs. For each source specific FSP, the LWG should list the constituents found in groundwater at that source (e.g. from the CSM documents prepared by the LWG) as well as the ranges in their concentrations. Justification as to why a chemical or class of chemicals found in groundwater at the source will not be analyzed should be provided. Specific changes to the analyte list are presented below:</p> <ul style="list-style-type: none"> • A full suite of metals should be analyzed at each site. This will not substantially increase either costs or sample volume requirements and is necessary as there are inorganics at some sites that may be at levels of concern (e.g., manganese at Arkema; Zn, Pb, Ni, Cr, and As at GASCO). • Cis-1,2- dichloroethene should be added to the VOC list as it is a major breakdown product of TCE and high concentrations are in groundwater at Siltronic. • Methyl naphthalene should be included in the list of PAHs. If feasible, dioxins and furans should be analyzed at Rhone Poulenc and Arkema. • Additional rationale should be provided to support the exclusion of certain sites from PAH and TPH analyses. 	The revised Table 4-1 presents the final analyte lists for each site as agreed upon for EPA conditional approval of the Addenda to this FSP.
A1	SC(43)	<p>Section 5 – Schedule: The schedule for implementation of the TZW FSP presents significant challenges. Groundwater discharge mapping results should be provided as quickly as possible in order to allow sufficient time for agency review. EPA comments on the first set of results should be incorporated into all subsequent data presentations.</p>	To facilitate resolution of comments and revisions to the FSP and the site-specific sampling addenda, meetings were held with EPA following delivery of each FSP addenda, to allow for efficient, in-person discussions and clarifications. The text has been updated to reference these meetings.